

**Poly[[bis(acetonitrile- $\kappa$ N)bis{ $\mu$ -2-[(2-carboxylatoethyl)ammoniomethyl]benzoato}copper(II)]bis(perchlorate) acetonitrile disolvate]**

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The reaction between the ligand *N*-(2-carboxybenzomethyl)- $\beta$ -alanine ( $H_2cbal$ ), obtained by reducing the Schiff base *N*-(2-carboxybenzomine)- $\beta$ -alanine, and copper(II) perchlorate afforded a copper(II) complex,  $\{[Cu_2(C_{11}H_{11}NO_4)_2(CH_3CN)_2](ClO_4)_2 \cdot 2CH_3CN\}_n$ , with an extended three-dimensional framework. The copper(II) ions are in a distorted square-pyramidal geometry in an  $O_4N$  coordination environment. There is a centre of inversion at the mid-point of the  $Cu \cdots Cu$  vector.

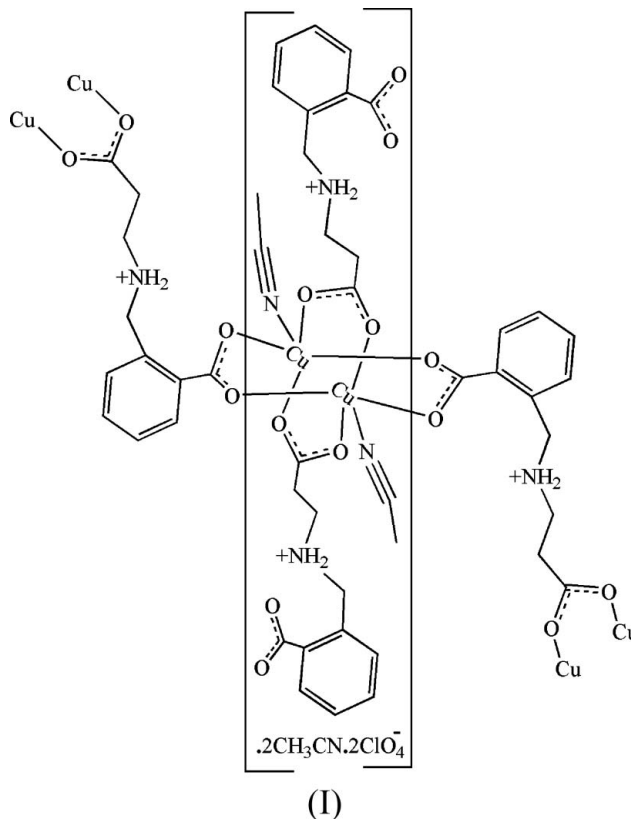
**Comment**

The coordination chemistry of copper(II) complexes has been the subject of extensive studies relevant to the active sites of many metalloproteins (Karlin & Tyeklar, 1993; Klinman, 1996) as well as the structural magnetochemistry of multi-metallic copper complexes (Kahn, 1993).

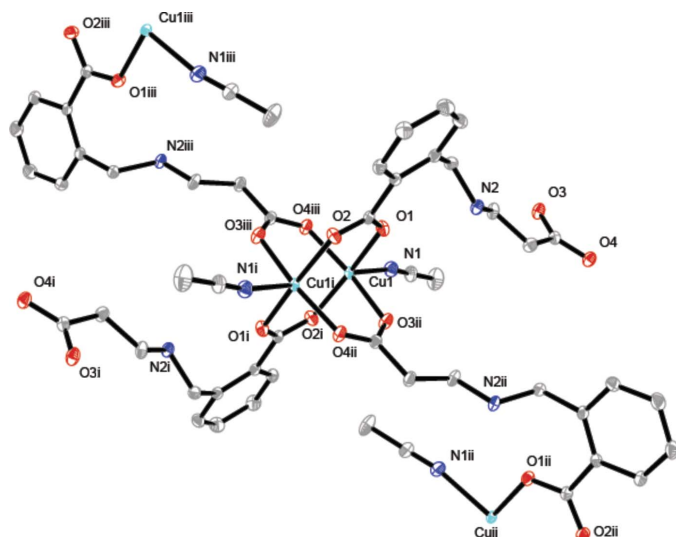
**Key indicators**

Single-crystal X-ray study  
 $T = 110\text{ K}$   
 Mean  $\sigma(C-C) = 0.002\text{ \AA}$   
 $R$  factor = 0.032  
 $wR$  factor = 0.080  
 Data-to-parameter ratio = 28.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.



A number of these complexes have been synthesized from ligands which contain analogous side groups to those found in proteins, such as carboxylate, as model compounds for multimetallic copper(II) enzymes such as haemocyanin and



**Figure 1**

The dinuclear unit of the polymeric structure of (I). Displacement ellipsoids are drawn at the 50% probability level. H atoms, solvent molecules and anions have been omitted for clarity. [Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x + \frac{1}{2}, -\frac{1}{2} + y, z$ ; (iii)  $x - \frac{1}{2}, y + \frac{1}{2}, z + 1$ .]

tyrosinase (Kitajima & Moro-oka, 1994). The methods adopted for the synthesis of these polynuclear copper complexes are usually related to the direct reaction of metal ions with multidentate ligands, coordination of monomeric copper complexes to other metal centres based on the noncovalent interaction, or multiple intermolecular interaction through efficient bridging ligands. Although binding mode and the bridging conformations, such as dicopper *syn,syn*, *syn,anti* and *anti,anti*, extend the structural versatility to form various structural systems (Tangoluis *et al.*, 1996), the crystal structure of the title complex, (I) (Fig. 1) shows the carboxylate groups are coordinated exclusively in a bridging mode.

The crystal structure of (I) shows that each  $\text{Cu}^{\text{II}}$  centre adopts a distorted square-pyramidal geometry, with an  $\text{NO}_4\text{Cu}$  coordination polyhedron. While the basal plane is defined by the O atoms from four carboxylate ligands, at the apex there is an N atom from acetonitrile used as solvent. Although the ligand,  $\text{H}_2\text{cbal}$ , has carboxylate and amine coordinating groups, the  $\text{Cu}^{\text{II}}$  atom is coordinated only by the carboxylate groups. The severity of the distortion is expressed by the deviation of the bond angles around  $\text{Cu}^{\text{II}}$  from the expected  $90^\circ$  for a regular geometry (Table 1). Since the first report of the crystal structure of dimeric copper(II) acetate monohydrate,  $\text{Cu}_2(\text{O}_2\text{CCH}_3)_4(\text{H}_2\text{O})_2$  (Van Niekerk *et al.*, 1953), a large number of similar copper(II) carboxylates have been reported in the literature. The  $\text{Cu}\cdots\text{Cu}$  distance of 2.6458 (3) Å observed in (I) is one of the examples of a short metal–metal internuclear distance with formal bond order of zero. A similar value (2.60 Å) has been reported (Boeyens *et al.*, 1985) based on a study of molecular mechanics calculations.

Selected geometric parameters for (I) are presented in Table 1. All other bonds and angles are within expected ranges (Allen *et al.*, 1997).

## Experimental

The title compound was prepared as follows. To a solution of  $\text{H}_2\text{cbal}$  [*N*-(2-carboxybenzomethyl)- $\beta$ -alanine] (0.223 g, 1.0 mmol), copper(II) perchlorate (0.223 g, 1.0 mmol) and NaOH (0.080 g, 2 mmol) in acetonitrile (20.0 ml) at room temperature was slowly added  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.370 g, 1.0 mmol) dissolved in methanol (10 ml). After stirring the reaction mixture for 10 min, the  $\text{H}_2\text{cbal}$  suspension became a homogenous blue–greenish solution. This was further stirred for 1 h and then filtered. X-ray quality green block-shaped single crystals of (I) were grown after 3 d by the slow diffusion of diethyl ether into the filtrate.

### Crystal data

$[\text{Cu}_2(\text{C}_{11}\text{H}_{11}\text{NO}_4)_2(\text{C}_2\text{H}_3\text{N})_2](\text{ClO}_4)_2 \cdot 2\text{C}_2\text{H}_3\text{N}$   
 $M_r = 934.65$   
 Orthorhombic, *Pbca*  
 $a = 16.7083$  (8) Å  
 $b = 10.9160$  (5) Å  
 $c = 21.0628$  (10) Å  
 $V = 3841.6$  (3) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.616$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 1.33$  mm<sup>-1</sup>  
 $T = 110$  (2) K  
 Irregular fragment, green  
 $0.14 \times 0.11 \times 0.10$  mm

### Data collection

Bruker SMART CCD area-detector 100962 measured reflections  
 diffractometer 7198 independent reflections  
 $\varphi$  and  $\omega$  scans 5483 reflections with  $I > 2\sigma(I)$   
 Absorption correction: multi-scan  $R_{\text{int}} = 0.048$   
 (SADABS; Sheldrick, 1996)  $\theta_{\text{max}} = 32.9^\circ$   
 $T_{\text{min}} = 0.839$ ,  $T_{\text{max}} = 0.882$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.080$   
 $S = 1.04$   
 7198 reflections  
 255 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 2.734P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.53$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.45$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

|  |             |  |             |
|--|-------------|--|-------------|
| $\text{Cu1}-\text{O2}^i$                     | 1.9576 (11) | $\text{Cu1}-\text{O1}$                 | 1.9754 (10) |
| $\text{Cu1}-\text{O3}^{iii}$                 | 1.9625 (11) | $\text{Cu1}-\text{N1}$                 | 2.1940 (13) |
| $\text{Cu1}-\text{O4}^{iii}$                 | 1.9698 (10) | $\text{Cu1}\cdots\text{Cu1}^i$         | 2.6458 (3)  |
| $\text{O2}^i-\text{Cu1}-\text{O3}^{iii}$     | 88.13 (5)   | $\text{O4}^{iii}-\text{Cu1}-\text{O1}$ | 90.51 (5)   |
| $\text{O2}^i-\text{Cu1}-\text{O4}^{iii}$     | 90.38 (5)   | $\text{O2}^i-\text{Cu1}-\text{N1}$     | 93.74 (5)   |
| $\text{O3}^{iii}-\text{Cu1}-\text{O4}^{iii}$ | 168.54 (4)  | $\text{O3}^{iii}-\text{Cu1}-\text{N1}$ | 92.41 (5)   |
| $\text{O2}^i-\text{Cu1}-\text{O1}$           | 168.02 (4)  | $\text{O4}^{iii}-\text{Cu1}-\text{N1}$ | 99.03 (5)   |
| $\text{O3}^{iii}-\text{Cu1}-\text{O1}$       | 88.64 (5)   | $\text{O1}-\text{Cu1}-\text{N1}$       | 97.92 (5)   |

Symmetry codes: (i)  $-x, -y + 1, -z + 1$ ; (ii)  $-x + \frac{1}{2}, y - \frac{1}{2}, z$ ; (iii)  $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$ .

All H atoms were included in calculated positions ( $\text{C}-\text{H} = 0.95$ ,  $0.98$  and  $0.99$  Å, and  $\text{N}-\text{H} = 0.92$  Å) and their isotropic displacement parameters were fixed [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$  or  $1.5U_{\text{eq}}(\text{C}_{\text{methyl}})$ ]. The methyl groups were allowed to rotate but not to tip.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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